PATENT SPECIFICATION

633,845

Convention Date (United States of America): Feb. 6, 1946.

Application Date (in United Kingdom): Nov. 19, 1946. No. 34230/46

Complete Specification Accepted: Dec. 30, 1949.

Index at acceptance:—Class 81(i), B11b5, N.

COMPLETE SPECIFICATION.

Improvements in or relating to Dentifrices

We, STERLING DRUG INC., a Corporation organised under the laws of the State of Delaware, United States of America, of 100, West 10th Street, Wilmington, Delaware, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to dentifrices.

Dentifrices are usually mixtures which serve to assist the toothbrush in cleaning the surfaces of the teeth. Such dentifrices contain a cleansing and polishing agent which largely constitutes the measure of value of the dentifrice. It is recognized that a certain amount of abrasiveness is a desirable characteristic of such agent. It is undesirable to employ an agent which is excessively abrasive due to deleterious effects produced on the teeth and tooth structure. On the other hand, too low an extent of abrasiveness renders the agent valueless for dentifricial purposes. While there is no exact mathematical relationship known between abrasiveness and cleansing action, it is generally accepted that the rapidity and effectiveness of the cleansing and polishing action bears some relation to the physical properties of the polishing agent.

Various polishing agents have heretofore been incorporated in dentifrices, including precipitated chalk, magnesium carbonate, oxide and hydroxide, kaolin, fullers earth, sodium borate and perborate and finely powdered pumice and silica. These agents have, moreover, been used in colloidal, hydrated and gel form. Most of these materials suffer from the disadvantage of being inordinately abrasive and certain of them, such as chalk, magnesium carbonate and oxide and calcium phosphate, leave a disagreeable chalky aftertaste or astrigent feeling in the mouth. The excessive abrasiveness of certain polishing agents is a function of relatively large particle size, angular particle shape and hardness. Some agents are so hard that they are inherently objectionable since they scratch the tooth surfaces and produce only a matte-like cleansing effect at best. Other agents are in the form of relatively large particles which tend to damage the tooth surface or structure and produce a matte-like effect particularly since such particles frequently have a shape which presents sharp points, acute angles and acicular configurations. In some instances no appreciable cleansing or polishing action is effected as in the case of liquid dentifrices because of deficient abrasive power. These and other related factors must be taken into account in compounding or formulating a dentifrice. It is for such reasons that existing dentifrices are either excessively abrasive and therefore inherently harmful, particularly when used one or more times daily as a part of a regular dental hygiene programme, or are of little or are of no appreciable value because of inadequate abrasiveness. There is, therefore, a difficult problem involved which has not been completely or satisfactorily solved so far as we are aware.

An object of this invention is to provide improved dentifrices having effective cleansing and polishing action without harmful effects on the teeth.

Another object of the invention is to incorporate in a dentifrice a cleansing and polishing agent having adequate but not excessive abrasiveness and having desirable qualities of particle size, particle shape and hardness.

A further object of the invention resides in a dentifrice which can be safely used one or more times daily and which is capable of imparting a high lustre to the surfaces of the teeth without adversely affecting the tooth enamel or the gums.

A still further object of the invention resides in the provision of a dentifrice, the essential cleansing and polishing component of which is comparatively soft and is in the form of small particles which are free from objectionably sharp points, acute angles and

[Price 2/-]

Price 25p

acicular configurations.

In accordance with the invention a dentifrice is provided comprising microcrystalline aluminium hydroxide and a dentifrice vehicle as hereinafter defined.

It has been found that the dentifrices provided in accordance with the invention containing microcrystalline aluminium hydroxide as an essential cleansing and polishing agent in which the particle size thereof is largely or substantially entirely submicroscopic, exhibit markedly different and exceptional properties with respect to cleaning, polishing and restoring natural lustre to teeth without causing objectionable abrasion or damaging the tooth enamel or structure even when used daily over an extended period of time.

The microcrystalline aluminium hydroxide which is employed in the dentifrices according to the invention has the chemical formula $Al(OH)_3$ and is a commercially available product, obtainable for example from the Aluminium Company of America. It exists in two crystalline modifications, the alpha form or hydrargillite and the beta form or bayehite. These crystalline forms are well-known to crystallographers, the alpha form comprising monoclinic prisms (Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green & Co., 1940, vol. V, p. 275), and the beta form having a metastable structure, which is in time transformed into the alpha form (Thorpe and Whitely, "Thorpe's Dictionary of Applied Chemistry," Longmans, Green & Co., 4th edition, 1937, vol. I, p. 284). Generally the two crystalline modifications are found together since the relative amounts of each depend upon the conditions of precipitation of the aluminium hydroxide. Microcrystalline aluminium hydroxide is odourless and tasteless. It is inert and insoluble in water, has good properties of absorption and is much less abrasive than precipitated chalk, which is usually employed as the standard for comparison.

As employed herein, the term "microcrystalline aluminium hydroxide" means those crystalline substances whose empirical formulæ correspond to $Al(OH)_3$ and which have an Al_2O_3 equivalent corresponding to approximately 50-66%. The term also includes both the alpha and the beta crystalline modifications as well as mixtures thereof. Aluminium hydroxide is distinct from and not to be confused with aluminium oxide (alumina) having the formula Al_2O_3 which is usually produced by the calcination of aluminium hydroxide to form a refractory material of entirely different crystal structure (Mellor, vol. V, p. 264) and which in its common forms is extremely hard and therefore unsuited for use in a dentifrice. Corundum and alundum are, respectively, examples of natural and calcined alumina which indicate clearly the unsuitability of such material for incorporation in dentifrices.

The particle size of the microcrystalline aluminium hydroxide plays an important part in making the same valuable for incorporation in dentifrices. We have found that aluminium hydroxide having a mean particle size below approximately 0.3 micron and having a distribution of particle sizes such that less than 5 to 10% of the particles are larger than 0.5 micron is especially efficacious. This is in sharp contrast with the size of particles of polishing agents in existing commercial dentifrices which are of comparatively large size. Seldom are particles of less than 1 micron in diameter encountered and the usual size is in the range of 2 to 10 microns. Sometimes a significant fraction of the cleaning and polishing agent particles in a dentifrice are as large as 30-50 microns in diameter. Such particle sizes have objectionable abrasive action, often feel gritty and are generally undesirable.

Aluminium hydroxide having the form and particle size referred to above, as an ingredient in dentifrice compositions, gives an excellent, hitherto unattainable lustre and polish to the surfaces of the teeth without harmful or damaging effects and without scratching or unduly abrading the teeth or tooth structure. Tests show that a mirror polish is produced by our new dentifrice in contrast to the ground-glass or matte type of surface which results from treatment with customary dentifrices and agents such as calcium carbonate and the calcium phosphates.

A representative sample of microcrystalline aluminium hydroxide upon examination for particle size under the electron microscope affords the following data:—

size, microns.	*%*	*% larger than size indicated.*
> 0.5	0.384	0.4
0.4 -0.5	2.115	2.5
0.3 -0.4	5.192	7.7
0.25 -0.3	4.807	12.5
0.2 -0.25	6.346	18.8
0.15 -0.2	8.846	27.7
0.1 -0.15	12.692	40.4
0.075-0.1	12.884	53.2
0.05 -0.075	22.5	75.7
0.025-0.05	22.115	97.9
< 0.025	2.115	99.99
	99.996	

From the above data it can be readily determined that the apparent mean particle size of this particular specimen of aluminium hydroxide is 0.103 micron.

The aluminium hydroxide which we use is essentially of such fine particle size as to be beyond the resolving power of the microscope. In other words, the particles are submicroscopic. A considerable fraction of

these particles are close to the limits of resolving power of the electron microscope. The smaller crystallites are so minute that they give diffuse x-ray diffraction patterns. These findings are best interpreted on the basis that the particles are loose agglomerates of crystallites, each of which may be composed of relatively few molecules, possibly 10 to 50 per crystallite. The larger particles give diffraction patterns characteristic of both the alpha and beta forms of aluminium hydroxide, indicating that a mixture of the two forms is present. The relative proportions of the two forms may vary considerably without affecting the efficacy of the polishing agent. The external form of these extremely fine particles is not readily determined. However, the term "microcrystalline aluminium hydroxide" as used herein includes such particles.

The individual crystallites of aluminium hydroxide are extremely small in size, being of the order of 0.001-0.01 micron in diameter. In agglomerates large enough for observation (0.1-0.5 micron in diameter) their external configuration approximates spherical symmetry. In other words the particles do not show an ellipsoidal or columnar form and no axis is significantly longer than any other axis. The particles are, accordingly, free from sharp points, acute angles and acicular configurations.

The hardness of the aluminium hydroxide particles is not directly measurable but it is known that they are relatively soft in nature and probably somewhat less than 2 to 3 on the Moh scale. It is believed to have a hardness of about two-thirds that of chalk and about one-half of that of aragonite, on the basis of the micro-crystals.

The microcrystalline aluminium hydroxide may be incorporated into dentifrice compositions in any suitable manner, depending upon whether a paste, powder, liquid, chewing gum or other dental preparation is to be produced. For this purpose we add appropriate proportions of one or more of the following ingredients, viz., surface-active agents, binders, excipients or plasticizers, flavouring materials, sweetening agents, colouring materials and lubricants. The various combinations of these ingredients may be conveniently termed dentifrice vehicles, adjuvants or bases (and are so referred to herein) and together with the polishing agent make up the dental paste, powder, liquid, chewing gum or other dental preparation.

The invention will now be further described with reference to the following examples which are intended as illustrative and hence do not limit the scope of the invention claimed. All parts are by weight.

EXAMPLE 1.

Tooth Powder.—90 parts of microcrystalline aluminium hydroxide having a mean particle size of approximately 0.1 micron and 0.1 part of saccharine are thoroughly mixed in a mechanical mixer such as a ribbon type powder mixer and sifter. Then 5 parts of powdered, neutral white soap are mixed in, followed by 3.5 parts of flavouring such as methyl salicylate.

EXAMPLE 2.

By proceeding in accordance with the directions of Example 1 but substituting 2 to 2.5 parts of a synthetic detergent such as sodium lauryl sulphoacetate instead of the soap a tooth powder is produced of eminently satisfactory nature differing from that resulting from Example 1.

EXAMPLE 3.

Tooth Powder.—The dentifrice of Examples 1 or 2 may be put in the form of small, discrete granules by procedures of generally known types. For example, an aqueous slurry prepared by mixing 50 parts of microcrystalline aluminium hydroxide, 2 parts of sodium lauryl sulphoacetate, 0.1 part of saccharin and 0.1 part of gum tragacanth may be dried by evaporation below 60°C., as by spray drying. The dried product is then screened until all granules pass through a 40 mesh screen and are retained by an 80 mesh screen.

EXAMPLE 4.

Tooth Paste.—90 parts of high grade propylene glycol (pharmaceutical quality) and 170 parts of 4% low-viscosity methyl cellulose solution are thoroughly mixed. Into the solution are stirred 0.5 part of saccharin and 4.5 parts of flavouring such as oil of birch. The resulting solution is added to 175 parts of microcrystalline aluminium hydroxide and the mass is mixed in a dough mixer and passed through a colloid mill.

EXAMPLE 5.

Tooth Paste.—A gel is formed of 1.5 parts of gum tragacanth and 50 parts of water. 64 parts of glycerin, 0.18 part of saccharin and 1.5 parts of flavouring such as oil of peppermint are added and mixed. 84 parts of microcrystalline aluminium hydroxide are mixed into the liquid, followed by 2 parts of powdered, neutral white soap. The resulting mass is put through a colloid mill.

EXAMPLE 6.

Liquid Dentifrice.—30 parts of microcrystalline aluminium hydroxide of substantially submicroscopic particle size is homogenized in a solution containing 5 parts of alcohol U.S.P., 3 parts of low-viscosity methyl cellulose, 3 part of sodium lauryl sulphate, and sufficient colouring, flavouring and water to make 80 parts of solution. The homogenization may be conveniently carried out in a blender of the Waring type.

From the foregoing illustrative examples it will be appreciated that the cleaning and polishing agent constitutes a major propor-

tion of the dentifrices in accordance with the invention and that, in the case of a powder dentifrice, the microcrystalline aluminium hydroxide is the predominating ingredient. Thus the dentifrices in accordance with the invention are characterized by being largely or, in some cases, almost wholly composed of the cleaning and polishing agent and thus differ markedly from dentifrices which utilize a very minor and often insignificant proportion of special polishing agents. The aluminium hydroxide content of the dentifrices in accordance with the invention ranges generally from about 25 to 30% in the case of liquid dentifrices to about 90 to 95% in the case of powders. The dentifrices enjoy the further advantage of being largely or almost wholly composed of an amphoteric material having no pronounced acid or basic qualities but being active and effective under alkaline, neutral and acid conditions.

Various modifications can be made from the foregoing examples without departing from the invention claimed. For instance, instead of soap, sodium lauryl sulphoacetate, sodium lauryl sulphate or some other surface-active agent could be used, such as the amine and metal salts of alkyl sulphates and sulphonated fatty alcohols, the amine and metal salts of aliphatic sulphonic acids and aliphatic-substituted aromatic sulphonic acids, the fatty acid amides of dialkylaminoalkylamines, basically substituted esters of fatty acids, and the like. Other flavouring materials may also be employed, including vanillin; oil of cinnamon, clove, anise, fennel, lavender and eucalyptus; thymol, menthol, camphor and other terpenes. Binders, excipients and lubricants that are satisfactory in the dentifrices that we contemplate comprise all such substances generally employed in such a manner, including gum karaya, Irish moss, gum acacia, agar-agar, salts of carboxymethyl cellulose, esters of polyhydroxy compounds such as sorbitol citrate, diethylene glycol diborate, mannitol oleate and the like, pectin, sorbitol syrup, corn starch, glycerite of starch, glycerite of sodium stearate, sodium alginate, gelatin, glycols, fatty acid esters of glycerine and glycols, mineral oil, petrolatum, alcohol and similar materials. Besides saccharin, other sweetening agents such as sugar, starch and sugar syrups, honey, dulcitol and lactose may be employed. Chicle or compositions of chicle and other chewing gum ingredients, such as corn syrup, form satisfactory bases for incorporating microcrystalline aluminium hydroxide in chewing gum.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A dentifrice comprising microcrystalline aluminium hydroxide and a dentifrice vehicle as hereinbefore defined.

2. A dentifrice comprising microcrystalline aluminium hydroxide and a dentifrice vehicle as hereinbefore defined, said microcrystalline aluminium hydroxide being in the form of agglomerates of crystallites having a mean diameter of not more than approximately 0.3 micron.

3. A dentifrice according to Claim 2, in which said microcrystalline aluminium hydroxide has a particle size averaging approximately 0.1 micron.

4. A dentifrice according to any of Claims 1 to 3, in the form of a powder and including a detergent.

5. A dentifrice according to any of Claims 1 to 3, in the form of a paste and including a surface-active agent and a plasticizer.

6. A dentifrice according to any of claims 1 to 3, in the form of a liquid dispersion and including a surface-active agent.

7. A dentifrice according to any of Claims 1 to 6, containing a major proportion of said microcrystalline aluminium hydroxide homogeneously admixed with said dentifrice vehicle.

8. A dentifrice according to any of Claims 1 to 7, in which said microcrystalline particles of aluminium hydroxide are characterized by freedom from acute angles, sharp points and acicular configurations, by being softer than chalk, and by being active under alkaline, neutral and acid conditions.

9. A dentifrice substantially as hereinbefore described with reference to the Examples.

Dated the 19th day of November, 1946.

For: STERLING DRUG INC.,
STEVENS, LANGNER, PARRY & ROLLINSON,
Chartered Patent Agents,
5/9, Quality Court, Chancery Lane, London, W.C.2, and at
120, East 41st Street, New York, 17, New York, U.S.A.

Printed for His Majesty's Stationery Office by Wickes & Andrews, Ltd., E.C.4. 39/244.—1950.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies, price 2s. 0d. each (inland), 2s. 1d. (abroad) may be obtained.